# Reversing Gels and Water Soluble Colloids from Aminosiloxanes

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**Abstract.** The unique sol/gel behavior of an organic/inorganic hybrid material synthesized from 3-aminopropyl-triethoxysilane (3AS) and tetramethoxysilane (TMOS) is discussed and examined. The addition of $H_2O$ to a mixture of a basic (3AS) and an acidic (TMOS) alkoxide leads to rapid gel formation. This wet gel reverses to a sol upon heating which is attributed to the dissolution of siloxane bonds between the surfaces of colloidal particles in the gel. The reversed sol dries to an optically transparent solid which is water soluble. The water solubility and the stability of these colloidal particles are described by their aminopropyl/silanol surface and the electrostatic interactions between them using DLVO theory.

**Keywords:** water soluble silica, colloids, 3-aminopropyltriethoxysilane, tetramethoxysilane, reversible gel, DLVO theory

## 1. Introduction

The gelation of colloidal silica can be pictured as the collision between colloids with silanol surfaces resulting in condensation reactions to form siloxane bonds. The siloxane bonds are formed irreversibly, and the resulting gel/precipitate is water-insoluble. Silica gels can be made water soluble: (1) by including substituents in the composition which prevent siloxane bond formation or (2) by placing the material in a highly basic environment where dissolution of the siloxane bonds can take place. Alkali metal silicates such as Na and K silicates [1] and certain organically modified sols are known to be water soluble [1, 2]. At a high pH, the silica surface will have a negative surface charge, and the positive cations (Na, K, Li, etc.) will adsorb on the surface of silica. Particles will then be linked together by acid-base bonds rather than siloxane bonds, and these materials can be peptized to become water soluble [1]. Organically modified sols can also be water soluble by incorporating organic ions on the surface of the silica such as tetramethylammonium ions [1, 3, 4], again preventing siloxane bond formation.

In this study, we present a new organically modified silicate material and discuss its unique characteristics of reversible gelation and water solubility which is believed to be governed by the dissolution of silica and electrostatic interactions between silica colloids.

## 2. Experimental

*Synthesis.* The physical behavior of the 3AS : TMOS composition during processing is shown in Fig. 1. Typically, 3AS, TMOS, and $H_2O$ (distilled or acidified) were mixed in a vial at a 5.5 : 1 : 3.9 mole ratio. Upon the addition of $H_2O$, rapid hydrolysis/condensation resulted in the formation of a wet gel (B) within 60 s of mixing with distilled $H_2O$ and within 10 s of mixing with acidified $H_2O$. This wet gel (B) was optically transparent, often with a bluish color caused by Raleigh scattering. Upon heating the wet gel to 75°C for several hours, the gel would reverse back to an optically transparent solution (C). The reversed solution (C) was slightly more viscous than the original 3AS : TMOS solution (A). Solution (C) was very stable, since it would not gel upon sitting or cooling. The drying of solution (C) resulted in an optically
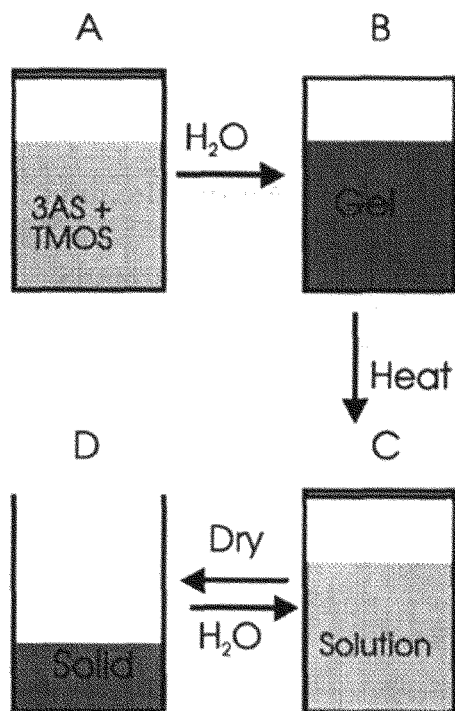
*Figure 1.* Schematic of the physical behavior of the 3AS : TMOS composition during processing.

transparent, crack free solid (D). The addition of water to the solid (D) returned the solid to a solution (C). The rate of dissolution was slow; it typically took several hours at 75°C.

*Atomic Force Microscopy (AFM).* The reversed solutions (C) were diluted in water and deposited and dried on mica. Images were taken in tapping mode on a Nanoscope III (Digital Instruments) AFM.

### 3. Results and Discussion

The formation of the wet gel (B) can be explained by examining the acid/base catalysis of the sol-gel reactions. As individual precursors, TMOS and 3AS hydrolyze rapidly within 30 s in the presence of water. Just after hydrolysis, these solutions are fluid, and do not form a gel as in the presently-studied (mixed) system. During typical sol-gel processing, treating an alkoxide in an acidic environment catalyzes both the hydrolysis and condensation reactions. The hydrolysis rate typically far exceeds the condensation rate, resulting in relatively long gel times [1, 5]. As the pH increases, the

condensation rate increases, decreasing the gel time. 3AS is an alkoxide with a basic amine substituent, while TMOS is a relatively acidic alkoxide. The addition of $H_2O$ to a mixture of an acid and a basic alkoxide results in rapid gel formation which is attributed to rapid catalysis of both hydrolysis (due to the acidic TMOS) and condensation (due to the basic 3AS).

The high optical transparency of the wet gel (B) suggests the rates of hydrolysis and condensation of the two alkoxides are closely matched and hence both of the alkoxides are being homogeneously incorporated into the matrix. By comparison, when $H_2O$ is added to a mixture of tetraethoxysilane (TEOS) and 3AS, or to a mixture of TMOS and 3-aminopropyltrimethoxysilane (3AMS), a precipitate is formed, suggesting that the reaction rates of the two alkoxides are not matched. The hydrolysis/condensation rate of TEOS is much slower than that of TMOS and the reaction rate of 3AMS is faster than that of 3AS [5, 6]. However, when water is added to TMOS and 4-aminobutyltriethoxysilane, which should have similar reaction rates as 3AS, an optically transparent initial gel is formed that behaves like the 3AS : TMOS composition.

The wet gel (B) reverses to a solution which contains colloidal particles (i.e., forms a sol); an AFM image of the colloidal particles (10–15 nm in diameter) is shown in Fig. 2(a) for a composition at 3AS : TMOS = 5.5. The gel-to-sol transition is probably caused by the dissolution of the siloxane crosslinks (i.e., the break up of Si—O—Si bonds by hydrolysis or reesterification reactions where solvent has easy access). The solubility of silica is known to increase at high pH [1, 5], and the large amine concentration in the present composition makes the gel very basic (pH = 9–10). Also, silica solubility increases by a factor of three upon increase in temperature from 25°C to 75°C [1], which coincides with the fact that the wet gel reversal rate increases with temperature.

The addition of different solvents in solution (A) provides some further evidence that dissolution of the silica is occurring during the gel-to-sol transition. Ethanol (EtOH) was added to the 3AS : TMOS mixture (A), and a gel was still formed when water was added. The ethanol containing gels still reversed and behaved like compositions without added solvent (Fig. 1). In contrast, 3AS : TMOS solutions in tetrahydrofuran (THF), also form an optically transparent gel (B), but the gels were found to be irreversible. Protic solvents, such as EtOH, can hydrogen bond to hydroxyl
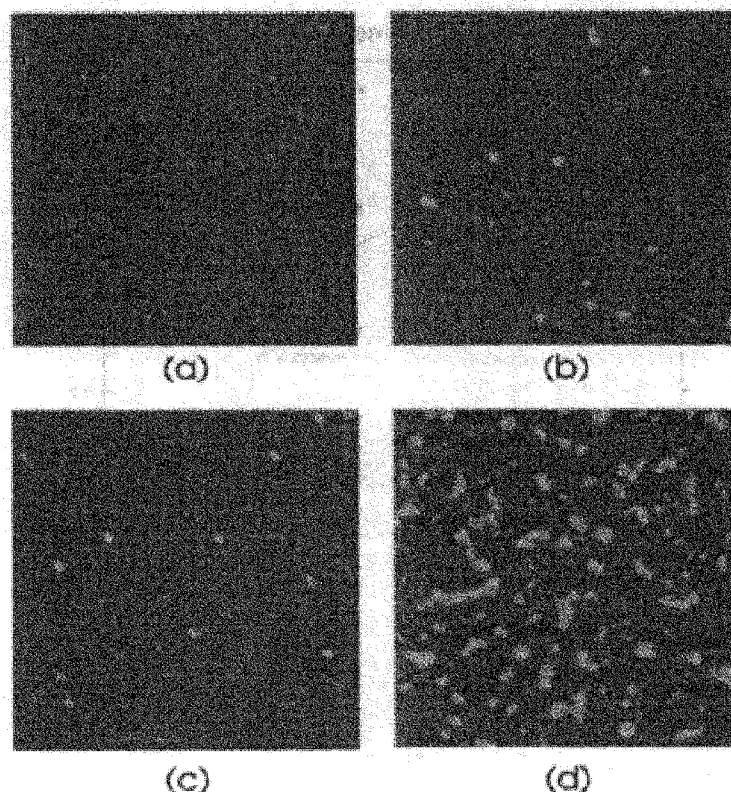
*Figure 2.* AFM images of diluted reversed solutions with (a) 3AS : TMOS = 5.5 at low concentrations, (b) 3AS : TMOS = 5.5 at higher concentrations, (c) 3AS : TMOS = 3 at low concentrations and (d) 3AS : TMOS = 3 at higher concentrations. The full scale for each image is 1000 nm.

ions or siloxanes to make them more electrophilic and can influence the reverse reactions as shown below [5]:



Aprotic solvents, such as THF or dioxane, are considerably more inert. They cannot form hydrogen bond with hydroxyl ions (or siloxanes) and cannot participate in the hydrolysis or reesterification of siloxane bonds. This supports the suggestion that the wet gel (B) formation is due to siloxane crosslinking as opposed to just hydrogen bonding, and the gel-to-sol reversal is due to the dissolution of silica.

A phase diagram for the 3AS + TMOS + H$_2$O system determined as a function of the acid content and the 3AS : TMOS ratio gives insight into the behavior of the gel (Fig. 3). In all cases, except at a 3AS : TMOS ratio of $\infty$, a wet gel (B) was formed. At lower acid contents and lower TMOS contents, the wet gels (B) were reversible. As the acid content increases, the de-

gree of hydrolysis/condensation of the alkoxides increases, thereby increasing the number of crosslinks between the colloidal particles. High crosslink densities decrease the ability for dissolution to cause breakup of the colloids and to cause gel reversal to a sol. As the TMOS content increases, the number of crosslink sites between the colloids should also increase, because TMOS is four functional and the 3AS is only three functional. At very high TMOS contents (3AS : TMOS < 2), the wet gel (B) did not reverse.

The reversed solutions (B) became more viscous with increasing TMOS content. This is believed to be caused by the increase in the colloid size and colloid interaction at higher TMOS contents as indicated by the AFM images in Fig. 2. At a 3AS : TMOS = 5.5 : 1 (Fig. 2(a)), the dispersed colloid size was relatively small (10–15 nm), while at 3AS : TMOS = 3 : 1 (Fig. 2(c)), the size was much larger (40–100 nm). There was also greater interaction between the colloids at 3AS : TMOS = 3 : 1, because at higher colloid concentrations, the colloid size increases dramatically (Fig. 2(d)). In contrast, with the 3AS : TMOS = 5.5 : 1
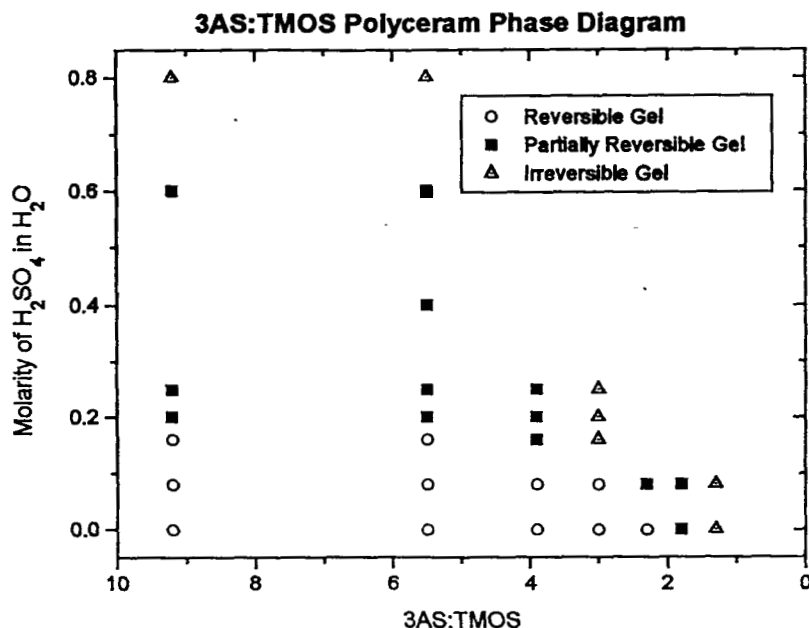
**3AS:TMOS Polyceram Phase Diagram**



*Figure 3.* Phase diagram of 3AS : TMOS compositions as a function of $H_2SO_4$ content and TMOS content.

composition, the colloid size does not increase as much (Fig. 2(b)). The greater interaction between the colloids of the higher TMOS samples could stem from the larger concentrations of silanols at the surface which can undergo condensation reactions (i.e., there are fewer amine groups to block the surface silanols).

3AS alone hydrolyzed by $H_2O$ is unusually stable in aqueous environments [7]. The unique water solubility stems from the formation of low molecular weight cage structures and from internal cyclization, where the propyl amine group wraps around and hydrogen bonds with the silanol groups [7, 8]. The propyl amine in this configuration blocks the silanol groups and hinders the condensation reactions, resulting in high stability in aqueous environments. The energy for cyclization has been reported to be $-26.3$ kcal/mole, which is much greater than the thermal energy [7]. When both 3AS and TMOS are hydrolyzed together, larger cage structures (colloids) are believed to be formed which are linked mostly by siloxane bonds in the wet gel (B). After dissolution, the reversed solution (C) does not return to a gel (B) upon cooling because: (1) the internal cyclization of the amine groups to the silanol groups on the surface of the colloids hinders inter-colloid condensation; and (2) the electrostatic interactions between the colloids contributes to the colloid-colloid repulsion (see discussion below). For these same reasons, the dried gel (D) is water soluble.

Two experiments confirm that the interaction of the colloidal particles is governed by electrostatic forces. First, the colloidal solution (B) precipated when $ZrCl_4$ was added to the solution. The addition of a multivalent salt contributed to the decrease in the electrical double layer and hence caused flocculation or coagulation. Second, the particles have a significant zeta potential of $-30$ to $-40$ mV as measured by electrophoresis, suggesting that a strong surface charge exists on the colloids.

Knowing this, Derjaguin-Landau-Verwey-Overbeek (DLVO) theory can be applied to confirm and predict conditions under which flocculation or dispersion of the colloids will occur [9]. DLVO theory takes into account electrostatic repulsion and van der Waals attraction and can be described by:

$$\kappa^{-1} = \left[ \left( \frac{4\pi}{\varepsilon\varepsilon_0 k_B T} \right) \cdot \left[ n_p Z_p^2 \, e^2 + n_\alpha Z_\alpha^2 \, e^2 \right] \right]^{\frac{1}{2}}$$

$$U_A = -\frac{A}{6} \cdot \left( \frac{2a_p^2}{r^2 - 4a_p^2} + \frac{2a_p^2}{r^2} + \ln\left( \frac{r^2 - 4a_p^2}{r^2} \right) \right)$$

$$U_R = \frac{Z^2 e^2}{\varepsilon\varepsilon_0} \cdot \left( \frac{\exp(\kappa a_p)}{1 + \kappa a_p} \right) \cdot \frac{\exp(-\kappa r)}{r}$$
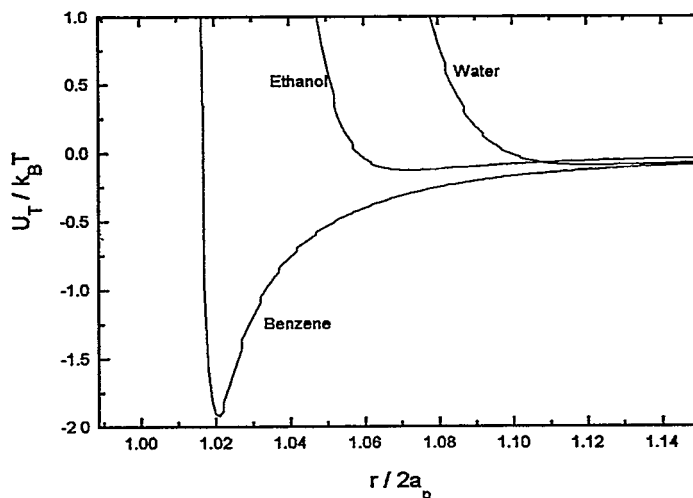
$$U_T = U_A + U_R$$

*Figure 4.* Interaction energy of two colloidal particles relative to the thermal energy predicted by DLVO theory (a) upon change in the dielectric constant of the solvent (for water $\varepsilon = 78$, $A = 0.323 * 10^{-20}$ J, for ethanol $\varepsilon = 26$ and $A = 0.181 * 10^{-20}$ J, for benzene $\varepsilon = 2$ and $A = 0.373 * 10^{-20}$ J) with the parameters $Z_p = 2500$, $a_p = 6$ nm, $T = 300$ K, $n_p = 10^{17}$ cm$^{-3}$, and $n_\alpha = Z * n_p$. Hamaker constants were estimated using equation 11.14 from Israelachvili [10].

where $\kappa^{-1}$ is the screening length (approximately the double layer thickness), $U_R$ is the Columbic repulsion energy, $U_A$ is the van der Waals attraction energy, $\varepsilon$ is the dielectric constant of the solvent, $\varepsilon_0$ is the permittivity of a vacuum, $k_B$ is Boltzmann's constant, $T$ is the temperature, $n_p$ is colloid density, $Z_p$ is valence of colloidal particle, $e$ is the charge of an electron, $n_\alpha$ is the counterion density, $Z_\alpha$ is the counterion valence, $a_p$ is the particle radius, $r$ is the distance between particles and $A$ is the Hamaker constant [9].

The reversed solution (C) was added to a variety of different solvents. In general, high dielectric solvents resulted in a stable colloid mixture, while low dielectric constant solvents result in flocculation of the colloidal particles. A decrease in the dielectric constant results in the decrease in the electrical double layer, and hence causes flocculation. Figure 4 is a plot of the energy between two colloids relative to the thermal energy for three solvents (H$_2$O ($\varepsilon = 78$), EtOH ($\varepsilon = 24$) and benzene ($\varepsilon = 2$)) as a function of distance between the colloids in units of particle diameter as predicted by DLVO theory. The low dielectric constant solvent, benzene, has a minimum in the energy curve suggesting that the colloids should flocculate; the curves for the two other solvents do not have an energy minimum, suggesting that the particles should be dispersed. The predicted behavior in Fig. 4 matched the experimental results of adding the

respective solvents, and therefore the behavior of the 3AS : TMOS colloids seems well predicted by DLVO theory.

## 4. Conclusions

A sol-gel material derived from 3AS and TMOS precursors has been characterized, and its unique properties of reversible gelation and water solubility have been described. The reversibility of the initial gel is caused by the dissolution of the Si—O—Si in the presence of a highly basic environment. This results in formation of colloidal particles with amine and silanol surfaces that are water soluble, and whose behavior is governed by electrostatic interactions.

## Acknowledgment

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